Molecular Hybrid Conducting/Magnetic Materials

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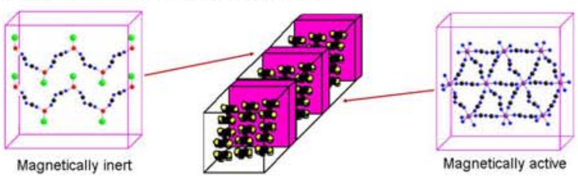
Motivation

- Hybrid conducting/magnetic materials with interactions between magnetic moments and delocalized conduction electrons could provide indirect RKKY-type magnetic coupling.
- Molecular-based networks are especially interesting because they are highly tunable and easier to process for applications.
- These materials provide model compounds for molecular-based spintronic materials where polarized electrons can be injected into conducting layers.

Goals

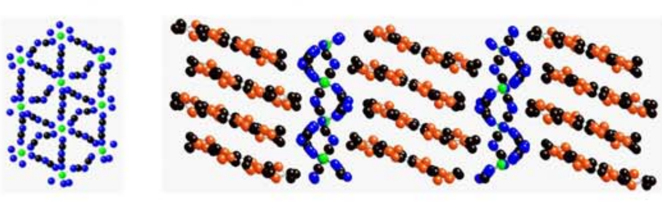
- Replace the magnetically inert anionic layer in charge transfer salts with magnetically active component.

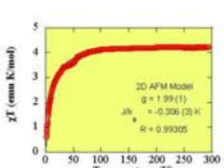


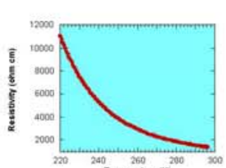
- Develop anionic $M(dca)_3^-$ [dca = dicyanamide, $N(CN)_2^-$] frameworks as potential magnetic components for hybrid systems.
  - Potential for strong magnetic superexchange.
  - Solubility permits growth of high quality single crystals and enables processing.
- Develop the structure/property relationships required to rationally design new materials with higher magnetic ordering temperatures.
- Increase coupling between:
  - Magnetic centers in anionic frameworks.
  - Magnetic and conductive layers in hybrid systems.
- Develop an understanding of the solution and growth dynamics of dca-based coordination polymers in order to control structural and physical properties of hybrid systems.

Hybrid Systems

- Crystallization and characterization of a hybrid charge transfer salt containing conductive organic layers separated by magnetic $M(dca)_3^-$ sheets.
  - Novel triangular anionic lattice (magnetic frustration).
  - Magnetic and conducting properties not yet optimal.



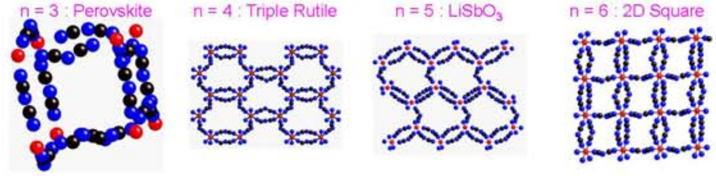




Magnetic Frameworks

- We have prepared a series of $[N(C_nH_{2n+1})_4M(dca)_3$ salts [M = divalent first row transition element] in which the size of the templating cation is incrementally increased.
  - Model compounds for developing structure/property relationships.
  - Precursors for synthesis of hybrid materials.

Novel Structures



- Minor changes in templating cation result in dramatic changes in arrangement of single/double dca bridges and topology.

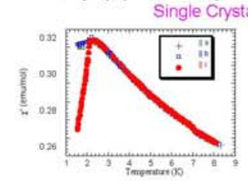
Novel Magnetism

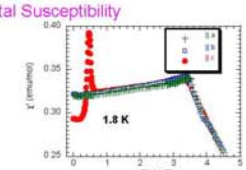
- First examples of long range magnetic ordering in $M(dca)_3^-$ systems.

$N(C_3H_7)_4Mn(dca)_3$

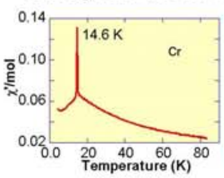
Large Single Crystals

Single Crystal Susceptibility





- The highest magnetic ordering temperatures have been obtained through the use of Cr^{+2}.



	$Mn(dca)_2$	$Cr(dca)_2$	(TBA)$Mn(dca)_3$	(TBA)$Cr(dca)_3$
T_N (K)	16	47	2	15
Bridge (atoms)	3	3	5	5
M-M (Å)	5.9	5.9	7.7	7.7
θ (K)	-3	-154	-2	-24

Significance

- The structure/property relationships developed in this work will be used to design new anionic magnetic frameworks that can be incorporated into more advanced hybrid materials.

Future Directions

- Incorporate other transition metals into magnetic frameworks:
  - Vanadium (higher magnetic ordering temperatures expected).
  - Second row elements (higher coordination numbers).
  - Bimetallic systems (ferrimagnetic interactions).
- Design the conductive layer in hybrid materials to possess:
  - Metallic properties.
  - Higher carrier concentrations.
  - Stronger couplings to magnetic lattice.
- Explore templating effect of selected cations:
  - Hydrogen bonding.
  - Cation radicals.
- Nanoscale confined systems.

See: Schlueter, J. A.; Manson, J. L.; Geiser, U. Inorg. Chem. 2005, 44, 3194-3202.

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